High Temperature Solvent Growth of a Sodium Gallium Silicate

Senior Thesis

by

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Abstract

A sodium gallium silicate probably $NaGaSiO_4$ has been synthesized by high temperature solvent growth.[4] This compound is probably a structural analogue of nepheline. It is hexagonal, possibly $P6_3$ a=8.63A c=8.35A. The crystals are clear, colorless, well-formed hexagonal prisms, devoid of cleavage, occasionally showing cruciform twins. The crystals are uniaxial(-) with indic es of refraction ω =1.540, ε =1.521.

Introduction

Investigations involving high temperature solvent crystal synthesis of scandium analogues of natural silicates (Ito and Frondel, 1968; Ito, 1977) gave rise to the idea that gallium analogues of natural silicates could be synthesized by similar methods.

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Method of Synthesis

The synthesis was carried out in a globar furnace regulated by a Barber-Coleman Wheelco controller with a 90% platinum-10% rhodium thermocouple. A Leeds-Northrup Millivolt Potentiometer was used to record actual temperature.

Reagents used:

Ga_2O_3 from Fairmount Chemical Co., Lot #13

Na_2CO_3 anhydrous granular analytical reagent from Mallinckrodt Chemical works #7528

SiO_2 Min-U-Sil

$Na_2MoO_4 \cdot 2H_2O$ Code 2277 from General Chemical Co. Lot #8

$NaVO_3$-meta, purified, from Matheson Coleman and Bell, CB1074, SX832

Stochiometric amounts of Ga_2O_3, Na_2O as Na_2CO_3, and SiO_2 for a composition $NaGaSi_2O_6$ were weighed on a Mettler balance. These constituents of the charge were mixed with the solvent (Na_2MoO_4 and $NaVO_3$) in a 1:15 ratio of charge to total solvent, Table 1. The solvent lowers the melting point, produces a more fluid melt and insures a proper liquidus phase (Grandin L'Eprevier, 1972). The thoroughly mixed charge and solvent was placed in a mullite crucible, covered, and heated gradually to 1122°C ± 15°C. The melt was kept at that temperature for 4 days to insure complete dissolution of the solid. The melt was then cooled slowly at 2.5°C per hour to 630°C. The crucible was then taken out of the furnace and air quenched to room temperature. The water soluble solvent was leached out by soaking the crucible in a beaker containing boiling double distilled water. Crystals with brilliant terminations were found encrusting the bottom and lower sides of the crucible. These crystals were then pried loose from the sides of the crucible by using a needle under a binocular microscope. Other synthesis attempts were made using varying amounts of solvent and charge, different temperatures and cooling rates and using a platinum crucible but with no further product.

Ga_2O_3	0.5g.
Na_2CO_3	0.283g.
SiO_2	0.641g.
$NaVO_3$	9.39g.
$NaMoO_4$	11.74g.
Soaking temp.	1122°C
Soaking time	4 days
Cooling rate	2.5°C/hr.
Cutoff Temp.	630°C
Crucible size	30ml.
Crystal size	max. 0.95mm.

Table 1. Synthesis data for Na-Ga Silcate

Crystal Studies

The crystals were simple hexagonal prisms with basal pinacoids with maximum size up to .95mm. x .35mm. x .30mm. Fig. 2. Bright curving faces on some crystals were observed as a result of numerous inclusions. Cross-shaped penetration twins with the twin plane $hh\bar{2}hl$, ρ near 45° were also observed. Similar cruciform twins have been observed in beryl.[1]

Microscopic Studies

Microscopic studies show the crystals to be clear, colorless, well- formed hexagonal prisms, devoid of cleavage; many bulging with inclusions in the central part of the crystal.

Optical Properties

Indices of refraction were determined by immersion using a Zeiss Abbe refractometer at room temperature using a sodium light source in part. After burnout of sodium light work was completed with white light. Table 2. The crystals are uniaxial(-). Anomalous biaxial character and flickery extinction was observable in strained crystals with numerous inclusions.

$\omega = 1.540 \pm .003$
$\varepsilon = 1.521 \pm .003$

Table 2. Indic es of Refraction

X-Ray Studies

Single crystal x-ray studies were carried out by oscillation, rotation and Weissenberg methods. The identity period c_o was determined by oscillation and rotation photographs around the c-axis. The identity period a_o was determined from the zero layer Weissenberg. Space group was not fully determined because equipment failure prevented making rotation and Weissenberg photographs around the a-axis. The zero, first and second layer Weissenberg

[1] Personal comm. H. E. Wenden

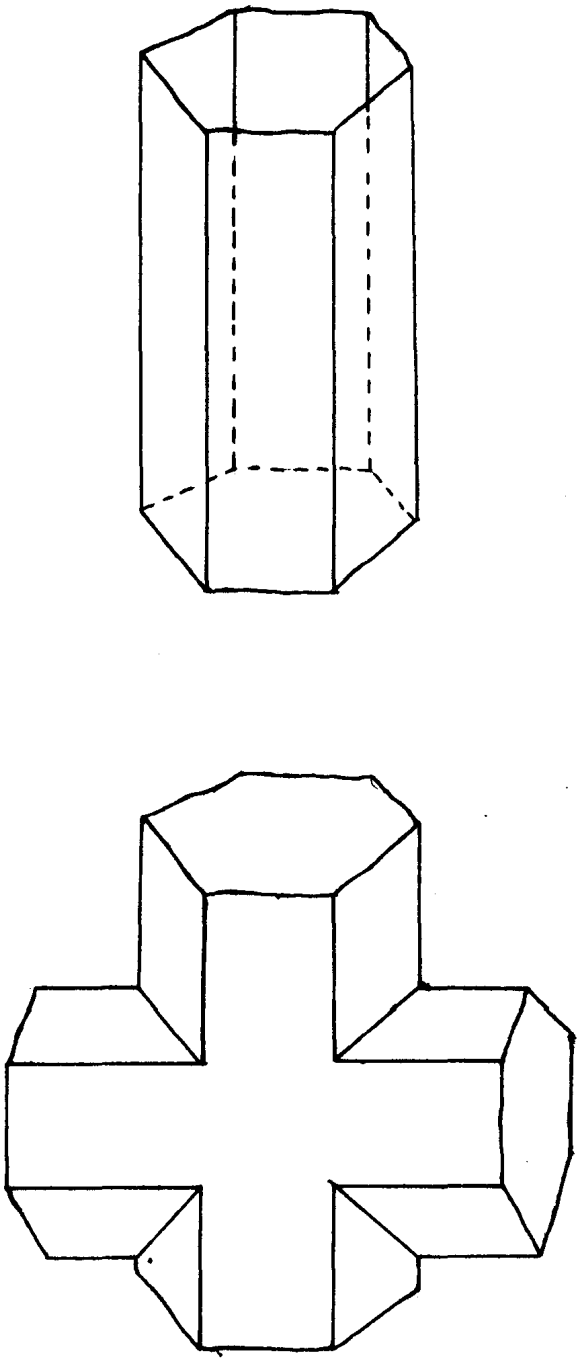

Figure 2. Simple hexagonal prism and cruciform twin as observed in synthesized sodium gallium silicate.

photographs around the c-axis indicates hexagonal symmetry, and the absence of any systematic omissions, hence P lattice. Table 3a&b Distinction between the numerous space groups consistent with the conditions observed requires additional information from an a-axis Weissenberg series.

Powder photographs were made in a 114.6mm. Norelco camera using filtered copper radiation. D-spacings were calculated by program x-ray by C. E. Corbató. Calculated and observed d-spacings are compared in Table 4.

The chemical composition of the crystals could not be determined because the large quantity of product needed for chemical analysis could not be obtained and electron microprobe facilities were not available.

a_o = 8.63A
c_o = 8.35A

Table 3a. Unit cell dimensions.

Conclusion

Synthesis of a new Na-Ga silicate provides evidence that other Ga^{+++} analogues of natural silicates can be synthesized. The Ga^{+++} analogue produced in the above research does not agree with any known compounds in the x-ray powder data file. Its symmetry, optical character and habit resemble nepheline but although c_o is similar, a_o is different. Table 5.

	Space Group	a_o	c_o	Opt. Sign	ω	ε
New Na-Ga Silicate	$P6_3$?	8.63	8.35	(-)	1.540	1.521
Nepheline	$P6_3$	10.01	8.41	(-)	1.547	1.527

Table 5.

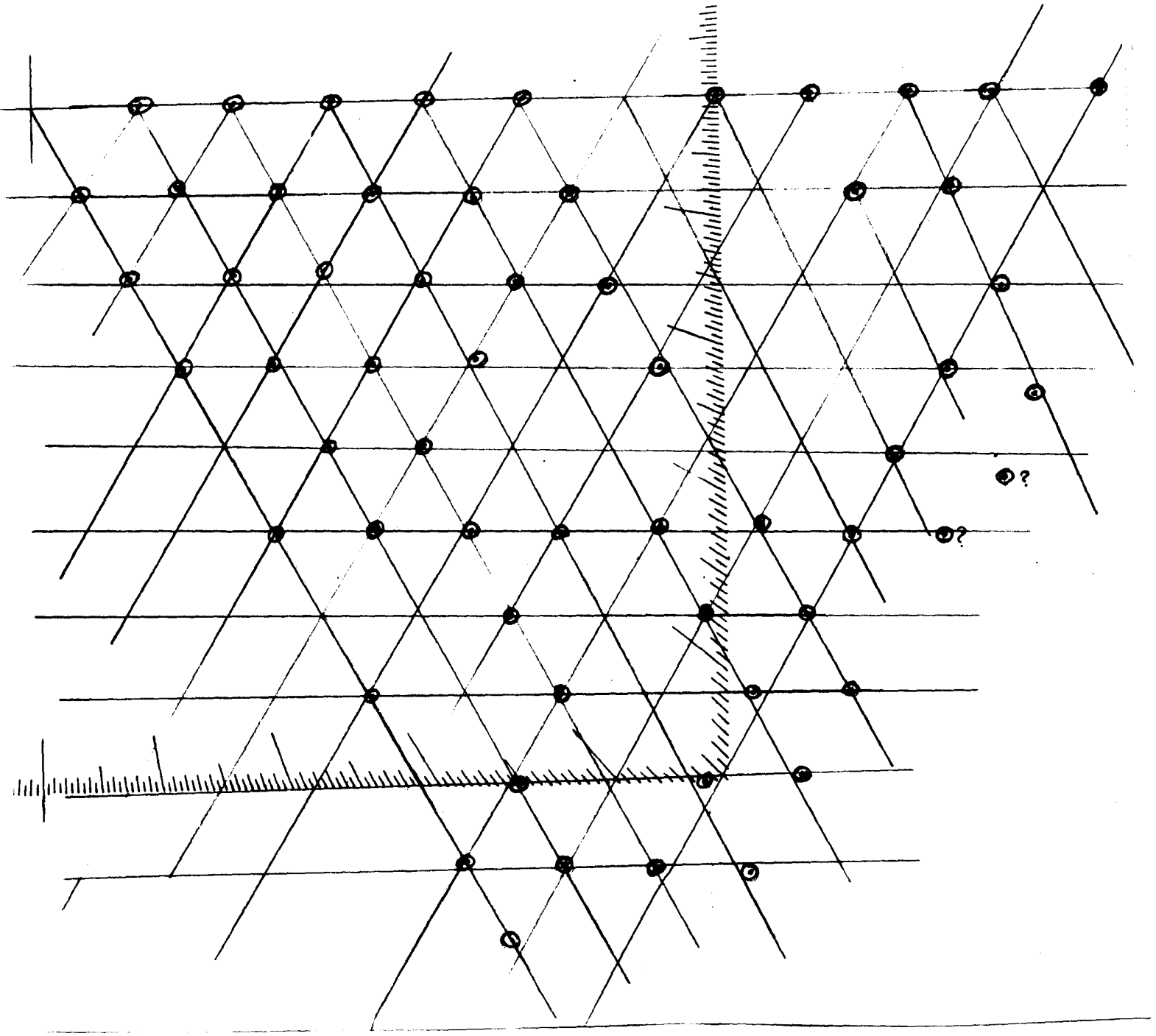

Table 3b. Gnomonic projection of synthesized sodium gallium silicate. Points from zero layer Weissenberg were used to construct this projection. Similar gnomonic projections were constructed from first and second layer Weissenbergs. These projections matched the zero layer projection exactly, thus showing absence of systematic omissions hence P lattice.

Table 4. X-ray powder pattern for synthetic sodium gallium silicate (CuK_{α} radiation)

h	k	l	d obs	d calc
0	0	1	8.67	8.35
1	0	0		7.47
1	0	1		5.57
			5.00	
			4.82 } ?	
			4.63	
1	1	0	4.33	4.32
0	0	2	4.19	4.18
1	1	1	3.84	3.83
2	0	0		3.74
1	0	2	3.62	3.64
2	0	1	3.41	3.33
			3.27 } ?	
			3.21	
1	1	2	3.01	3.00
2	1	0	2.89	2.82
2	0	2		2.78
0	0	3		2.78
2	1	1		2.68
1	0	3	2.58	2.61
3	0	0	2.50	2.49
3	0	1	2.40	2.39
2	1	2	2.34	2.34
1	1	3		2.34
			2.31	
2	0	3		2.23
2	2	0		2.16
3	0	2		2.14
2	2	1	2.09	2.08
0	0	4		2.08
3	1	0		2.07
3	1	1		2.01
1	0	4		2.01
			1.99	
2	1	3		1.98

h	k	l	d obs	d calc
2	2	2	1.93	1.92
1	1	4		1.88
4	0	0		1.87
3	1	2		1.86
3	0	3		1.86
4	0	1	1.82	1.82
2	0	4		1.82
			1.73	
3	2	0		1.71
4	0	2		1.70
2	2	3		1.70
3	2	1	1.69	1.68
2	1	4		1.68
0	0	5		1.68
3	1	3		1.67
4	1	0	1.62	1.63
1	0	5		1.63
4	1	1		1.60
3	0	4		1.60
3	2	2		1.59
1	1	5	1.56	1.56
4	0	3		1.55
2	0	5	1.52	1.52
4	1	2		1.52
2	2	4		1.50
5	0	0		1.49
5	0	1	1.47	1.47
3	1	4		1.47
3	2	3	1.46	1.46
3	3	0		1.44
2	1	5	1.43	1.44
3	3	1		1.42
4	2	0		1.41
5	0	0		1.41
4	1	3		1.41

Table 4 (cont.)

h	k	l	d obs	d calc
4	2	1		1.39
4	0	4	1.39	1.39
0	0	6		1.39
3	0	5		1.39
1	0	6	1.37	1.37
3	3	2		1.36
5	1	0		1.34
4	2	2		1.34
5	1	1	1.33	1.33
3	2	4		1.33
1	1	6		1.32
2	2	5	1.32	1.32
5	0	3		1.32
2	0	6		1.30
3	1	5		1.30
4	1	4		1.28
5	1	2	1.28	1.28
3	3	3		1.28
4	2	3		1.26
2	1	6		1.25
6	0	0	1.24	1.24
4	0	5		1.24
6	0	1		1.23
4	3	0		1.23
4	3	1		1.22
5	0	4		1.22
3	0	6		1.22
5	1	3		1.21
5	2	0	1.20	1.20
3	2	5		1.20
6	0	2		1.19
0	0	7		1.19
5	2	1		1.18
3	3	4	1.18	1.18
4	3	7		1.18
1	0	7		1.18
4	2	4		1.17
2	2	6		1.17
4	1	5		1.17
3	1	6		1.16
5	2	2		1.15
1	1	7		1.15
6	1	0		1.14
6	0	3	1.14	1.14
2	0	7		1.14
6	1	1		1.13
5	1	4		1.13
4	3	3		1.12
4	0	6		1.12
5	0	5		1.11
6	1	2		1.11
5	2	3		1.11
2	1	7		1.11

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